REMARKS/ARGUMENTS

Claims 1 and 4-22 are pending.

Claims 1 and 9 have been amended.

Claims 2-3 have been cancelled.

Claims 12-22 have been added.

Support for the amendments is found in the claims and specification (e.g., pages 3, 4, 5, 7 8, 9, 10, 11), as originally filed. No new matter is believed to have been added.

Applicants wish to thank the Examiners for a meeting on November 10, 2008. Possible amendments to overcome the rejections were discussed. The Examiners indicated that introducing the limitation of claim 5 into claim 1 would likely overcome the art rejections.

In response to the objection to the specification, Applicants have amended the title and submitted a new abstract. Applicants have also submitted with this paper a clean and marked-up copies of the substitute specification to comply with the USPTO requirements. No new matter is believed to have been added. Applicants request that the objections to the specification be withdrawn.

The Examiner is of the opinion that "a monomer conversion of $\geq 95\%$ by weight" should be "a monomer conversion of $\leq 95\%$ by weight." Applicants respectfully disagree. A second paragraph on page 2 of the specification describes that an emulsion polymerization rate usually decreases sharply and a time of occupying a reactor increases significantly with decreasing a monomer concentration. Therefore, to avoid a long occupancy time of the reactor, a polymerization reaction is not carried to achieve a full conversion, but is carried to more than 95% but less than 99.98% (less than the full conversion). The polymerization is

then switched to a different initiator that is more active at a residual polymerization. Thus, "a

monomer conversion of $\geq 95\%$ by weight" is correct.

In response to the rejection of Claim 9 under 35 U.S.C. 112, second paragraph,

Applicants have deleted the trademarks from the claim. Applicants request that the rejection

be withdrawn.

Claims 1-4, 6-8, and 10 are rejected under 35 U.S.C. 102() as being anticipated by

Mishima et al., US 3,951,925. The rejection is traversed because Mishima et al. do not

describe a free radical aqueous emulsion (oil-in-water) polymerization comprising (a)

initiating a monomer polymerization with a water-soluble initiator at a starting temperature

T_S (or below the end reaction temperature T_E) at which an oil-soluble initiator has a half-life

of ≥ 10 hours, (b) metering at least the monomer and the water-soluble initiator into a

reaction mixture while the temperature is raised from T_S to T_E, and (c) conducting a residual

polymerization with the oil-soluble initiator at T_E at which has a half-life of the oil-soluble

initiator is ≤ 5 hours.

The claimed method

The claimed invention is directed to a one step polymerization process of aqueous

polymer dispersions producing a low residual monomer content and having a high conversion

rate (page 3 of the present specification).

(i) At least a oil-soluble initiator, water and a dispersant are mixed at a starting

temperature T_S or lower. Monomers and a water-soluble initiator may or may not be added to

the mixture.

(ii) The obtained mixture is heated to the temperature T_S (e.g., if the temperature is

lower than T_S) and the monomers (the total amount or the remaining amount) are

continuously metered into the mixture. The total or main amount of the water-soluble initiator is also added to the mixture.

(iii) The polymerization is started by the water-soluble initiator at T_S and the temperature is raised from T_S to T_E and the monomers are continuously fed into the reaction mixture while the temperature is raised. The oil-soluble initiator is inactive at the starting reaction temperature (i.e., the oil-soluble initiator has a half-life of $\geq$ 10 hours at the starting reaction temperature T_S) and becomes more active as a temperature approaches the end reaction temperature at which the oil-soluble initiator is fully active (i.e., a half-life of $\leq$ 5 hours at the end reaction temperature T_E). Polymer particles are formed during this stage of polymerization. The oil-soluble initiator is also a part of the particles.

(iv) Thus, when the reaction temperature reaches the temperature T_E, the oil-soluble initiator becomes fully active and a residual polymerization of unreacted monomer units (e.g., within the polymer particles) is carried out by the oil-soluble initiator.

As illustrated by the Examples of the present specification, the claimed one-step process produces aqueous polymer dispersions having a low residual monomer content (pages 18-20). For example, the Example on pages 17-18 shows that 5% of the feed I was initially added at 20-25°C and heated to 95 °C. On reaching 95 °C, the remaining amount of the feed I and the total amount of feeds II and II were metered in with constant feed streams during 90 min.

<div align="center">The disclosure of Mishima et al.</div>

Mishima et al. describe an aqueous suspension <u>batch</u> polymerization of water-insoluble vinyl chloride polymers (abstract). The suspension polymerization of Mishima et al. is conducted in the presence of an oil-soluble initiator, a monomer, water, and dispersions (see col. 1-3). All components are added in full without metering. After the initial polymerization in the presence of oil-soluble initiators (step one), a further polymerization is

<div align="center">10</div>

conducted after a water-soluble initiator has been added (step two) (col. 2, lines 30-36 and 54-63;col. 3-4, the bridging paragraph). The oil-soluble initiator is *deactivated* (end of step one) before adding the water-soluble initiator (step two) (col. 3-4, the bridging paragraph). Mishima et al. describe that the reaction temperature should be 30-70°C (col. 3, lines 33-36). Mishima et al.'s polymerization is conducted at 52°C by the oil-soluble initiator and then the water soluble-initiator was added to continue the polymerization at the same temperature (Example 1). Thus, the Mishima et al. reaction is a batch polymerization, is conducted in two steps at the same temperature, is initiated by the oil-soluble initiator and is continued by the water-soluble initiator to proceed inside the pores on the surface of the polyvolyl chloride particles formed by the oil-soluble inhibitor (col. 2, lines 21-37).

Comparison of the claimed invention and the process of Mishima et al.

Mishima et al. do not describe (a) initiating a monomer polymerization with a water-soluble initiator at a starting temperature T_S at which an oil-soluble initiator has a half-life of ≥ 10 hours, (b) metering at least the monomers and the water-soluble initiator into the mixture while the temperature is raised from T_S to T_E, and (c) conducting a residual polymerization with the oil-soluble initiator at T_E at which has a half-life of the oil-soluble initiator is ≤ 5 hours.

Mishima et al. do not describe that the oil-soluble initiator is inactive at the starting reaction temperature and becomes more active as a temperature approaches the end reaction temperature at which the oil-soluble initiator is fully active.

In addition, Mishima et al. do not describe that $30°C \leq T_S \leq 120°C$ and $80°C \leq T_E \leq 200°C$ (claim 5).

Thus, Mishima et al. do not anticipate the claimed process. Applicants request that the rejection be withdrawn.

Claims 5 and 9 are rejected under 35 U.S.C. 103(a) over Mishima et al. and Robinson et al., US 4,739,008. The rejection is traversed because the combination of the references does not describe or suggest:

A) a free radical aqueous emulsion polymerization comprising(a) initiating a monomer polymerization with a water-soluble initiator at a starting temperature T_S (or below the end reaction temperature T_E) at which an oil-soluble initiator has a half-life of $\geq$ 10 hours, (b) metering at least the monomer and the water-soluble initiator into a reaction mixture while the temperature is raised from T_S to T_E, and (c) conducting a residual polymerization with the oil-soluble initiator at T_E at which has a half-life of the oil-soluble initiator is $\leq$ 5 hours;

B) $30°C \leq T_S \leq 120°C$ and $80°C \leq T_E \leq 200°C$ (claim 5); and

C) combining the processes of Mishima et al. and Robinson et al., is technically improper because the processes are fundamentally different.

The disclosure of Mishima et al. is describe above.

Robinson et al. do not cure the deficiency of Mishima et al.

Robinson et al. describe a *water-in-oil bi-phase* initiator system (compare to the *oil-in-water* emulsion of the claimed process) (col. 1, lines 35-47). Robinson et al. describe a batch polymerization (no metering of a water-soluble initiator and monomers as in the claimed process) (see the Examples). Robinson et al. describe that the bi-phase initiator system is a combination of either (i) an oil-soluble initiator and a water-soluble initiator or a water-soluble activator and a oil-soluble initiator; or (ii) a water-soluble initiator and an oil-soluble activator (col. 1, lines 35-47). Thus, the Robinson et al. system can comprise an oil-soluble initiator and a water-soluble activator.

The Comparative Example in the present specification comprises an oil-soluble initiator and a water-soluble activator (feed III on page 20) (similar to the combination in (ii)

of Robinson et al., col. 3, lines 35-47). The aqueous polymer dispersion obtained in the Comparative Example is inferior.

Robinson et al.'s monomer is water-soluble, the system is a water-in-oil bi-phase system, the process is a batch polymeriszation, and a water-soluble initiator is not added during feeding monomers. Thus, Robinson et al. do not describe the claimed process.

Further, combining Robinson et al. and Mishima et al. (a) is improper and (b) still does not produce the claimed process.

Robinson et al. describe the polymerization of water-soluble polymers in a stable water-in-oil emulsion which comprises an oil-soluble and water-soluble initiator simultaneously. Robinson et al. describe a broad range of the polymerization temperatures of -20°C to 200°C and 0°C to 100°C (col. 7, lines 46-48) but suggest selecting the polymerization at 35-45°C (outside of the range of present claim 5) (Example 1).

The Examiner is of the opinion that modifying the polymerization of water-insoluble polymers of Mishima et al. with the temperature of the polymerization of Robinson et al. for water-soluble polymers would have been obvious.

In response, it is noted that the polymerization processes of Mishima et al. and Robinson et al. are fundamentally different. Mishima et al. describe a polymerization process for water-insoluble polymers, wherein at the first stage an oil-soluble initiator is used for forming particles of vinyl chloride polymer in a state of suspension (col. 2, lines 27-36). After a lapse of a specified period of time, a water-soluble initiator is added to allow polymerization by means of the water-soluble initiator to proceed inside the pores or on the surfaces of the polyvinyl chloride particles formed earlier in the oil-soluble initiated polymerization (col. 2, lines 27-36).

Mishima et al. explicitly describe that the polymerization temperature is in the range of 30-70°C. Mishima et al. also explicitly describe that oil-soluble and water-insoluble initiators are added sequentially for different types of polymerization (co l. 2, lines 27-36). Robinson et al. describe a process of polymerization of water-soluble polymers in water-in-oil bi-phase system when oil and water initiators are added simultaneously to form an emulsion for further polymerization of the water-soluble polymers. Robinson et al. describe that the polymerization temperature is from -20 to 200°C.

The goal of Mishima et al. is to provide polymerization of water-insoluble particles to high degree [see Table 1] wherein the high percent of polymerization is from 88 to about 90%.

Introducing a high temperature (80-200°C of claim 5) into the polymerization of water-insoluble polymers of Mishima et al. would not have been expected to provide a high polymerization yield of water-insoluble polymers because Mishima et al. specifically determines that the reaction temperature should be 30-70°C.

One could not have expected to improve or maintain the polymerization degree of the water-insoluble polymers of Mishima et al. when temperature had been raised from 30 to 70 °C as recommended by Mishima et al. to about 80-200°C because Mishima et al. and Robinson et al. provide specific polymerization conditions for fundamentally different polymers (water-insoluble v. water-soluble).

Thus, Mishima et al. and Robinson et al. do not make the claimed process obvious. Applicants request that the rejection be withdrawn.

Claim 11 is rejected under 35 U.S.C. 103(a) over Mishima et al. and Humkey et al., US 3, 920,624. The rejection is traversed because the combination of the references does not describe or suggest a free radical aqueous emulsion polymerization comprising (a) initiating a

monomer polymerization with a water-soluble initiator at a starting temperature T_S (or below the end reaction temperature T_E) at which an oil-soluble initiator has a half-life of $\geq$ 10 hours, (b) metering at least the monomer and the water-soluble initiator into a reaction mixture while the temperature is raised from T_S to T_E, and (c) conducting a residual polymerization with the oil-soluble initiator at T_E at which has a half-life of the oil-soluble initiator is $\leq$ 5 hours.

The disclosure of Mishima et al. is describe above.

Humkey et al. do not cure the deficiency of Mishima et al.

Humkey et al. describe stripping residual volatiles from polymer pellets (abstract).

Humkey et al. do not describe a free radical aqueous emulsion polymerization comprising (a) initiating a monomer polymerization with a water-soluble initiator at a starting temperature T_S (or below the end reaction temperature T_E) at which an oil-soluble initiator has a half-life of $\geq$ 10 hours, (b) metering at least the monomer and the water-soluble initiator into a reaction mixture while the temperature is raised from T_S to T_E, and (c) conducting a residual polymerization with the oil-soluble initiator at T_E at which has a half-life of the oil-soluble initiator is $\leq$ 5 hours.

Substituting the process of Humkey et al. into that of Mishima et al. still does not produce the claimed process.

Thus, Humkey et al. and Mishima et al. do not make the claimed process obvious. Applicants request that the rejection be withdrawn.

A Notice of Allowance for all pending claims is requested.

Respectfully submitted,

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TITLE OF THE INVENTION

METHOD FOR PRODUCING AQUEOUS POLYMER DISPERSIONS

BACKGROUND OF THE INVENTION

5   FIELD OF THE INVENTION

The present invention relates to a process for the preparation of an aqueous polymer dispersion by free radical aqueous emulsion polymerization of at least one ethylenically unsaturated compound (monomer) in the presence of at least one dispersant~~, wherein~~

~~a)   in a reaction vessel at a temperature which is less than or equal to the starting~~

10   ~~reaction temperature T_S,~~

~~a_1)   at least one portion of demineralized water,~~

~~a_2)   at least one portion of at least one oil-soluble free radical initiator,~~

~~a_3)   at least one portion of at least one dispersant,~~

~~a_4)   if appropriate, a portion of the at least one monomer and~~

15   ~~a_5)   if appropriate, a portion of at least one water-soluble free radical initiator are~~

~~initially taken, thereafter~~

~~b)   the reaction mixture obtained is, if appropriate, heated to the starting reaction~~

~~temperature T_S, thereafter~~

~~c)   the following are metered into the reaction mixture:~~

20   ~~c_1)   if appropriate, the remaining amount of demineralized water,~~

~~c_2)   if appropriate, the remaining amount of the at least one oil-soluble free radical~~

~~initiator,~~

~~c_3)   if appropriate, the remaining amount of the at least one dispersant,~~

~~c_4)   the total amount or if appropriate, the remaining amount of the at least one~~

25   ~~monomer and~~

~~c_5)   the main amount of the at least one water-soluble free radical initiator, and~~

~~d)   the reaction mixture is heated to an end reaction temperature T_E during the~~

~~metering of the at least one monomer.~~

The present invention also relates to the aqueous polymer dispersions obtainable by

30   the novel process, the use thereof as binders in adhesives, sealing compounds, plastics renders, paper coating slips and surface coating materials and for modifying mineral binders.

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Aqueous polymer dispersions (latices) are generally known. They are fluid systems which comprise polymer coils consisting of a plurality of entangled polymer chains (i.e. polymer particles) as the disperse phase in an aqueous dispersing medium. The weight average diameter of the polymer particles is frequently from 10 to ~~5 000~~ 5,000 nm.

As in the case of polymer solutions on evaporation of the solvent, aqueous polymer dispersions, on evaporation of the aqueous dispersing medium, have the potential for forming polymer films and are therefore used in particular as binders. Owing to their environmentally friendly properties, they are becoming increasingly important.

The preparation of aqueous polymer dispersions is frequently carried out by free radical aqueous emulsion polymerization [cf. for example Encyclopedia of Polymer Science and Engineering, Vol. 8, page 659 et seq. (1987); D. C. Blackley, in High Polymer Latices, Vol. 1, page 35 et seq. (1966); H. Warson, The Applications of Synthetic Resin Emulsions, page 246 et seq., Chapter 5 (1972); D. Diederich, Chemie in unserer Zeit, 24, (1990), 135 to 142; Emulsion Polymerisation, Interscience Publishers, New York (1965); DE-A 40 03 422, and Dispersionen synthetischer Hochpolymerer, F. Holscher, Springer-Verlag, Berlin 1969]. A characteristic of this process is that water-soluble free radical initiators are used as polymerization catalysts.

For reasons relating to apparatus, the free radical aqueous emulsion polymerization is frequently carried out at below 100°. Since the polymerization rates [corresponding to the instantaneous monomer conversion rate] decrease sharply with decreasing monomer concentration and, on the other hand, the operation times of the polymerization reactors, which for reaction safety reasons are equipped with expensive instrumentation, are to be minimized, the polymerization reaction in the polymerization vessel is frequently carried out only to a monomer conversion of ≥95% by weight. The conversion of the remaining monomers is then effected in a downstream polymerization step in a separate reactor generally equipped with less expensive instrumentation. As a rule, this postpolymerization is carried out using a free radical initiator or free radical initiator system optimized for these purposes. Examples of free radical initiators which are particularly suitable for the postpolymerization or reduction of residual monomer contents are to be found in EP-B 003 957, EP-B 028 348, EP-B 563 726, EP-A 764 699, U.S. Pat. No. 4,529,753, DE-A 37 18 520, DE-A 38 34 734, DE-A 42 32 194, DE-A 195 29 599, WO 95/33775, EP-A 767 180, DE-A 19839199 or DE-A 19840586.

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In addition, WO 00/22003 discloses a one-stage process for the preparation of aqueous polymer dispersions having a low residual monomer content, in which process the polymerization reaction is initiated by a redox initiator system and the polymerization temperature is specified by a defined temperature profile. A disadvantage of this process is

5   that, in addition to the oxidizing agent acting as a free radical initiator, it is essential for a reducing agent to be present, by means of which the polymerization temperature can be reduced but through which additional foreign components also enter the aqueous polymer dispersions, which foreign components generally cannot be removed from the aqueous polymer dispersion even by subsequent stripping with inert gas or with steam.

10   Against the background of the prior art, it is an object of the present invention to provide a further one-stage process for the preparation of aqueous polymer dispersions having a low residual monomer content, which process, however, manages without additional reducing agents.

15   SUMMARY OF THE INVENTION

The present invention relates to a process for the preparation of an aqueous polymer dispersion by free radical aqueous emulsion polymerization of at least one ethylenically unsaturated compound (monomer) in the presence of at least one dispersant, wherein

a)   in a reaction vessel at a temperature which is less than or equal to the starting

20   reaction temperature T_S,

a_1)   at least one portion of demineralized water,

a_2)   at least one portion of at least one oil-soluble free radical initiator,

a_3)   at least one portion of at least one dispersant,

a_4)   optionally, a portion of the at least one monomer and

25   a_5)   optionally, a portion of at least one water-soluble free radical initiator are

initially taken, thereafter

b)   the reaction mixture obtained is, optionally, heated to the starting reaction

temperature T_S, thereafter

c)   the following are metered into the reaction mixture:

30   c_1)   optionally, the remaining amount of demineralized water,

c_2)   optionally, the remaining amount of the at least one oil-soluble free radical

initiator,

c_3)   optionally, the remaining amount of the at least one dispersant,

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c4)   the total amount or optionally, the remaining amount of the at least one monomer and

c5)   the main amount of the at least one water-soluble free radical initiator, and

d)   the reaction mixture is heated to an end reaction temperature T_E during the metering of the at least one monomer.

DETAILED DESCRIPTION OF THE INVENTION

We have found that this object is achieved by the process defined at the outset.

For the preparation of the aqueous polymer dispersions, ethylenically unsaturated compounds which can be subjected to free radical polymerization in a simple manner, for example ethylene, vinylaromatic monomers, such as styrene, .alpha.-methylstyrene, o-chlorostyrene or vinyltoluenes, vinyl halides, such as vinyl chloride or vinylidene chloride, esters of vinyl alcohol and monocarboxylic acids of 1 to 18 carbon atoms, such as vinyl acetate, vinyl propionate, vinyl n-butyrate, vinyl laurate and vinyl stearate, esters of α,β-monoethylenically unsaturated mono- and dicarboxylic acids, preferably of 3 to 6 carbon atoms, in particular acrylic acid, methacrylic acid, maleic acid, fumaric acid and itaconic acid, with alkanols of in general 1 to 12, preferably 1 to 8, in particular 1 to 4, carbon atoms, in particular methyl, ethyl, n-butyl, isobutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl and 2-ethylhexyl acrylate and methacrylate, dimethyl or di-n-butyl fumarate and maleate, nitriles of α,β-monoethylenically unsaturated carboxylic acids, such as acrylonitrile, methacrylonitrile, fumaronitrile, maleonitrile, and conjugated C_{4-8}-dienes, such as 1,3-butadiene (butadiene) and isoprene, are particularly suitable as at least one monomer. Said monomers are as a rule the main monomers, which together account for more than 50, preferably more than 80, % by weight, based on the total amount of monomers. As a rule, these monomers have only moderate to low solubility in water under standard conditions [20°C, 1 bar (absolute)].

Monomers which have high water solubility under the abovementioned conditions are those which comprise at least one acid group and/or the corresponding anion thereof or at least one amino, amido, ureido or N-heterocyclic group and/or the ammonium derivatives thereof which are protonated or alkylated on the nitrogen. Examples are α,β-monoethylenically unsaturated mono- and dicarboxylic acids of 3 to 6 carbon atoms and the amides thereof, e.g. acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, acrylamide and methacrylamide, and furthermore vinylsulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, styrenesulfonic acid and the water-soluble salts thereof and N-vinylpyrrolidone, 2-vinylpyridine, 4-vinylpyridine, 2-vinylimidazole, 2-(N,N-

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dimethylamino)ethyl acrylate, 2-(N,N-dimethylamino)ethyl methacrylate, 2-(N,N-diethylamino)ethyl acrylate, 2-(N,N-diethylamino)ethyl methacrylate, 2-(N-tert-butylamino)ethyl methacrylate, N-(3-N',N'-dimethylaminopropyl)methacrylamide and 2-(1-imidazolin-2-onyl)ethyl methacrylate. Usually, the abovementioned monomers are present only as modified monomers in amounts of less than 10, preferably less than 5, % by weight, based on the total amount of monomers.

Monomers which usually increase the internal strength of the films of the polymer matrix usually have at least one epoxy, hydroxyl, N-methylol or carbonyl group, or at least two nonconjugated ethylenically unsaturated double bonds. Examples of these are monomers having two vinyl radicals, monomers having two vinylidene radicals and monomers having two alkenyl radicals. Particularly advantageous are the diesters of dihydric alcohols with α,β-monoethylenically unsaturated monocarboxylic acids, among which acrylic and methacrylic acid are preferred. Examples of such monomers having two nonconjugated ethylenically unsaturated double bonds are alkylene glycol diacrylates and dimethacrylates, such as ethylene glycol diacrylate, 1,2-propylene glycol diacrylate, 1,3-propylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butylene glycol diacrylates and ethylene glycol dimethacrylate, 1,2-propylene glycol dimethacrylate, 1,3-propylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butylene glycol dimethacrylate, and divinylbenzene, vinyl methacrylate, vinyl acrylate, allyl methacrylate, allyl acrylate, diallyl maleate, diallyl fumarate, methylenebisacrylamide, cyclopentadienyl acrylate, triallyl cyanurate or triallyl isocyanurate. Also of particular importance in this context are the C_1-C_8-hydroxyalkyl methacrylates and acrylates, such as n-hydroxyethyl, n-hydroxypropyl or n-hydroxybutyl acrylate and methacrylate, and compounds such as diacetoneacryamide and acetylacetoxyethyl acrylate and methacrylate. Frequently, the abovementioned monomers are used in amounts of up to 10, preferably less than 5, % by weight, based in each case on the total amount of monomers.

Aqueous polymer dispersions which can be particularly advantageously prepared according to the invention are those whose polymers comprise

-	from 50 to 99.9% by weight	of esters of acrylic and/or methacrylic acid with alkanols of 1 to 12 carbon atoms and/or styrene, or
-	from 50 to 99.9% by weight	of styrene and/or butadiene, or
-	from 50 to 99.9% by weight	of vinyl chloride and/or vinylidene chloride, or
-	from 40 to 99.9% by weight	of vinyl acetate, vinyl propionate and/or ethylene

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incorporated in the form of polymerized units.

Aqueous polymer dispersions which in particular can be prepared according to the invention are those whose polymers comprise

-	from 0.1 to 5% by weight	of at least one α,β-monoethylenically unsaturated mono- and/or dicarboxylic acid of 3 to 6 carbon atoms and/or the amide thereof and
-	from 50 to 99.9% by weight	of at least one ester of acrylic and/or methacrylic acid with alkanols of 1 to 12 carbon atoms and/or styrene, or
-	from 0.1 to 5% by weight	of at least one α,β-monoethylenically unsaturated mono- and/or dicarboxylic acid of 3 to 6 carbon atoms and/or the amides thereof and
-	from 50 to 99.9% by weight	of styrene and/or butadiene, or
-	from 0.1 to 5% by weight	of at least one α,β-monoethylenically unsaturated mono- and/or dicarboxylic acid of 3 to 6 carbon atoms and/or the amide thereof and
-	from 50 to 99.9% by weight	of vinyl chloride and/or vinylidene chloride, or
-	from 0.1 to 5% by weight	of at least one α,β-monoethylenically unsaturated mono- and/or dicarboxylic acid of 3 to 6 carbon atoms and/or the amide thereof and
-	from 40 to 99.9% by weight	of vinyl acetate, vinyl propionate and/or ethylene

5   incorporated in the form of polymerized units.

Dispersants which keep both the monomer droplets and polymer particles dispersed in the aqueous phase and thus ensure the stability of the aqueous polymer dispersion produced are concomitantly used in the novel process. Suitable such dispersants are both the protective colloids usually used for carrying out free radical aqueous emulsion polymerizations and

10   emulsifiers.

Suitable protective colloids are, for example, polyvinyl alcohols, cellulose derivatives or vinylpyrrolidone-comprising copolymers. A detailed description of further suitable protective colloids is to be found in Houben-Weyl, Methoden der organischen Chemie, Volume XIV/1, Makromolekulare Stoffe, pages 411 to 420, Georg-Thieme-Verlag, Stuttgart,

15   1961.

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Mixtures of emulsifiers and/or protective colloids can of course also be used. Emulsifiers whose relative molecular weights, in contrast to the protective colloids, are usually below ~~1 000~~ 1,000 are frequently exclusively used as dispersants. They may be anionic, cationic or nonionic. Where mixtures of surface-active substances are used, the

5   individual components must of course be compatible with one another, which in case of doubt can be checked by means of a few preliminary experiments. In general, anionic emulsifiers are compatible with one another and with nonionic emulsifiers. The same also applies to cationic emulsifiers, whereas anionic and cationic emulsifiers are generally not compatible with one another.

10   Customary emulsifiers are, for example, ethoxylated mono-, di- and trialkylphenols (degree of ethoxylation: from 3 to 50, alkyl radical: C_4 to C_{12}), ethoxylated fatty alcohols (degree of ethoxylation: from 3 to 50; alkyl radical: C_8 to C_{36}) and alkali metal and ammonium salts of alkylsulfates (alkyl radical: C_8 to C_{12}), of sulfuric monoesters of ethoxylated alkanols (degree of ethoxylation: from 4 to 30, alkyl radical: C_{12} to C_{18}) and of

15   ethoxylated alkylphenols (degree of ethoxylation: from 3 to 50, alkyl radical: C_4 to C_{12}), of alkylsulfonic acids (alkyl radical: C_{12} to C_{18}) and of alkylarylsulfonic acids (alkyl radical: C_9 to C_{18}). Further suitable emulsifiers are to be found in Houben-Weyl, Methoden der organischen Chemie, Volume XIV/1, Makromolekulare Stoffe, pages 192 to 208, Georg-Thieme-Verlag, Stuttgart, 1961.

20   Compounds of the formula I

(I),
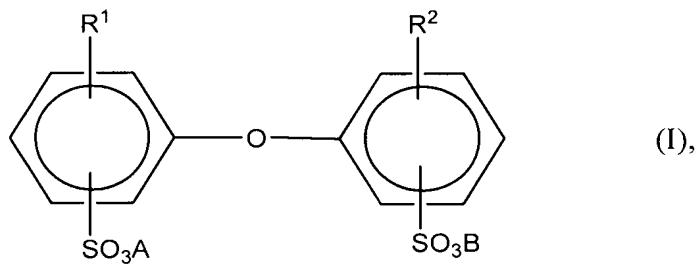
where R^1 and R^2 are C_4- to C_{24}-alkyl and one of the radicals R^1 or R^2 may also be hydrogen,

25   and A and B may be alkali metal ions and/or ammonium ions, have furthermore proven to be surface-active substances. In the formula I, R^1 and R^2 are preferably linear or branched alkyl radicals of 6 to 18, in particular 6,12 or 16, carbon atoms or H atoms, R^1 and R^2 not both simultaneously being H atoms. A and B are preferably sodium, potassium or ammonium ions, sodium ions being particularly preferred. Compounds I in which A and B are sodium

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ions, R^1 is a branched alkyl radical of 12 carbon atoms and R^2 is an H atom or R^1 are particularly preferred. Industrial mixtures which contain from 50 to 90% by weight of monoalkylated product, for example ~~Dowfax~~DOWFAX® 2A1 (brand of Dow Chemical Company), are frequently used.

5   The compounds I are generally known, for example from U.S. Pat. No. 4,269,749, and are commercially available.

Nonionic and/or anionic emulsifiers are preferably used for the novel process. However, cationic emulsifiers may also be used.

As a rule, the amount of dispersant used is from 0.1 to 5, preferably from 1 to 3, % by

10   weight, based in each case on the total amount of the monomers to be subjected to the free radical polymerization (total amount of monomers).

Characteristic for the novel process is that both water-soluble and oil-soluble free radical initiators are used. Water-soluble free radical initiators are as a rule understood as meaning all those free radical initiators which are usually used in free radical aqueous

15   emulsion polymerization, while oil-soluble free radical initiators are understood as meaning all those free radical initiators which a person skilled in the art usually uses in free radical solution polymerization. In this document, water-soluble free radical initiators are understood as meaning all those free radical initiators which have a solubility of $\geq 1\%$ by weight at 20°C and atmospheric pressure in demineralized water, while oil-soluble free

20   radical initiators are understood as meaning all those free radical initiators which have a solubility of <1% by weight under the abovementioned conditions. Frequently, water-soluble free radical initiators have a water solubility of ≥ 2, ≥ 5 or $\geq 10\%$ by weight under the abovementioned conditions, while oil-soluble free radical initiators frequently have a water solubility of ≤ 0.9, ≤ 0.8, ≤ 0.7, ≤ 0.6, ≤ 0.5, ≤ 0.4, ≤ 0.3, ≤ 0.2 or $\leq 0.1\%$ by weight.

25   The water-soluble free radical initiators may be, for example, both peroxides and azo compounds. Peroxides which may be used are in principle inorganic peroxides, such as hydrogen peroxide, or peroxodisulfates, such as the mono- or di-alkali metal or ammonium salts of peroxodisulfuric acid, for example the mono- and disodium, mono- and dipotassium or ammonium salts, or organic hydroperoxides, such as alkyl hydroperoxides, for example

30   tert-butyl, p-menthyl or cumyl hydroperoxide. Azo compounds used are substantially 2,2'-azobisisobutyronitrile and 2,2'-azobis(amidinopropyl) dihydrochloride (AIBA, corresponds to V-50 from Wako Chemicals).

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A mono- or di-alkali metal or ammonium salt of peroxodisulfuric acid, for example dipotassium peroxydisulfate, disodium peroxydisulfate or diammonium peroxydisulfate, is preferably used as the water-soluble free radical initiator. Of course, it is also possible to use mixtures of the abovementioned water-soluble free radical initiators.

5   The total amount of water-soluble free radical initiator used is from 0.01 to 5, frequently from 0.5 to 3, often from 1 to 2, % by weight, based in each case on the total amount of monomers.

What is essential to the process is that the at least one water-soluble free radical initiator is selected so that it is capable of initiating a free radical polymerization reaction of

10   the at least one monomer at the starting reaction temperature T_S.

Examples of oil-soluble free radical initiators are dialkyl and diaryl peroxides, such as di-tert-amyl peroxide, dicumyl peroxide, bis(tert-butylperoxyisopropyl)benzene, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, tert-butyl cumyl peroxide, 2,5-bis(tert-butylperoxy) -2,5-dimethyl-3-hexene, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(tert-

15   butylperoxy)cyclohexane, 2,2-bis(tert-butylperoxy)butane or di-tert-butyl peroxide, aliphatic and aromatic peroxyesters, such as cumyl peroxyneodecanoate, 2,4,4-trimethylpentyl 2-peroxyneodecanoate, tert-amyl peroxyneodecanoate, tert-butyl peroxyneodecanoate, tert-amyl peroxypivalate, tert-butyl peroxypivalate, tert-amyl peroxy-2-ethylhexanoate, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxydiethylacetate, 1,4-bis(tert-

20   butylperoxy)cyclohexane, tert-butyl peroxyisobutanoate, tert-butyl peroxy-3,5,5-trimethylhexanoate, tert-butyl peroxyacetate, tert-amyl peroxybenzoate or tert-butyl peroxybenzoate, dialkanoyl and dibenzoyl peroxides, such as diisobutanoyl peroxide, bis(3,5,5-trimethylhexanoyl) peroxide, dilauroyl peroxide, didecanoyl peroxide, 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane or dibenzoyl peroxide, and peroxycarbonates,

25   such as bis(4-tert-butylcyclohexyl) peroxydicarbonate, bis(2-ethylhexyl) peroxydicarbonate, di-tert-butyl peroxydicarbonate, diacetyl peroxydicarbonate, dimyristyl peroxydicarbonate, tert-butyl peroxyisopropylcarbonate or tert-butyl peroxy-2-ethylhexylcarbonate.

A compound selected from the group consisting of tert-butyl peroxy-2-ethylhexanoate (~~Trigonox~~TRIGONOX® 21), tert-amyl peroxy-2-ethylhexanoate, tert-butyl peroxybenzoate

30   (~~Trigonox~~TRIGONOX® C), tert-amyl peroxybenzoate, tert-butyl peroxyacetate, tert-butyl peroxy-3,5,5-trimethylhexanoate (~~Trigonox~~TRIGONOX® 42 S), tert-butyl peroxyisobutanoate, tert-butyl peroxydiethylacetate, tert-butyl peroxypivalate, tert-butyl peroxyisopropylcarbonate, (~~Trigonox~~TRIGONOX® BPIC) and tert-butyl peroxy-2-ethylhexylcarbonate (~~Trigonox~~TRIGONOX® 117) is preferably used as at least one oil-

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soluble free radical initiator. It is of course also possible to use mixtures of the abovementioned oil-soluble free radical initiators.

The total amount of oil-soluble free radical initiator used is from 0.01 to 5, frequently from 0.5 to 3, often from 1 to 2, % by weight, based in each case on the total amount of

5   monomers.

The oil-soluble free radical initiator is advantageously chosen so that it has a half-life of ≥ 10, frequently ≥ 12, often ≥ 15, hours at the starting reaction temperature T_S and a half-life of ≥ 5, frequently ≤ 3, hours, often ≤ 1 hour, at the end reaction temperature T_E. The corresponding half-lives are familiar to a person skilled in the art or can be determined by

10   him in simple experiments. Corresponding reference works are also available, for example J. Brandrup, E. H. Immergut and E. A. Grulke, Polymer Handbook, 4th edition, Chapter II, pages 1 to 76, J. Wiley & Sons, New York.

It is essential to the process that at least one portion of demineralized water, at least one portion of at least one oil-soluble free radical initiator, at least one portion of at least one

15   dispersant, if required a portion of the at least one monomer and, if appropriate optionally, a portion of at least one water-soluble free radical initiator are initially taken in a reaction vessel at a temperature which is less than or equal to the starting reaction temperature T_S, frequently at from 20 to 25°C (room temperature).

At least a portion of the demineralized water is initially taken in the reaction vessel.

20   However, it is also possible initially to take the total amount of the water in the reaction vessel. If only a portion of the water is initially taken, the remaining amount of the water can be added to the reaction medium during the metering phase, separately or advantageously together with the at least one monomer, in particular in the form of an aqueous monomer emulsion. Frequently, the amount of water initially taken in the reaction vessel is ≤ 50, ≤ 30,

25   ≤ 20 or $\leq 10\%$ by weight, based in each case on the total amount of water. The total amount of water is such that the aqueous polymer dispersion obtained has a solids content of from 20 to 70, frequently from 30 to 65, often from 40 to 60, % by weight.

Furthermore, at least one portion of the at least one dispersant is initially taken in the reaction vessel. However, it is also possible initially to take the total amount of the dispersant

30   in the reaction vessel. If only a portion of the dispersant is initially taken, the remaining amount of the dispersant can be added to the reaction medium during the metering phase, separately or advantageously together with the at least one monomer, in particular in the form of an aqueous monomer emulsion. Frequently, the amount of dispersant initially taken in the

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reaction vessel is ≤50, ≤30, ≤20 or ≤10% by weight, based in each case on the total amount of dispersant.

In addition, at least one portion of the at least one oil-soluble free radical initiator is also additionally taken in the reaction vessel. However, it is also possible initially to take the total amount of the oil-soluble free radical initiator in the reaction vessel. If only a portion of the oil-soluble free radical initiator is initially taken, the remaining amount of the oil-soluble free radical initiator can be added separately to the reaction medium during the metering phase. Frequently, the amount of the oil-soluble free radical initiator initially taken in the reaction vessel is ≥50, ≥70, ≥80 or ≥90% by weight, based in each case on the total amount of the oil-soluble free radical initiator. Preferably, the total amount of the at least one oil-soluble free radical initiator is initially taken in the reaction vessel.

Optionally, a portion of the at least one monomer can also be initially taken. If this is the case, the amount of the at least one monomer initially taken in the reaction vessel is ≤50, ≤30, ≤20, ≤10 or ≤5% by weight, based in each case on the total amount of monomer. Optionally, ≤10 or ≤5% by weight, based in each case on the total amount of monomers, of monomers are preferred.

Moreover, a portion of the at least one water-soluble free radical initiator can optionally also be initially taken. If this is the case, the amount of the at least one water-soluble free radical initiator initially taken in the reaction vessel is ≤30, ≤20, ≤10 or ≤5% by weight, based in each case on the total amount of the at least one water-soluble free radical initiator. Optionally, ≤10 or ≤5% by weight, based in each case on the total amount of water-soluble free radical initiators, of water-soluble free radical initiators are preferred. Frequently, no water-soluble free radical initiator is initially taken in the reaction vessel.

As in all free radical polymerization reactions, it is advantageous if the initial introduction of the reaction components, of the metering/polymerization and the subsequent reaction in the reaction vessel are carried out under an inert gas atmosphere, for example under a nitrogen or argon atmosphere.

If the temperature at which the reaction components are initially taken in the reaction vessel is less than the starting reaction temperature T_S, for example room temperature, the reaction mixture is heated to the starting reaction temperature T_S with stirring and under an inert gas atmosphere and, ~~if appropriate~~ optionally, is left at this temperature for some time. This is advantageous in particular when portions of monomers and water-soluble free radical initiator were initially taken in the reaction vessel. The duration is frequently chosen so that

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it is at least sufficient for initiating the polymerization reaction, which as a rule is detectable from the liberation of heat of polymerization. The same also applies if the abovementioned components are initially taken at the starting reaction temperature T_S.

~~If appropriate~~Optionally, the remaining amount of demineralized water, ~~if appropriate~~
5   optionally, the remaining amount of the at least one oil-soluble free radical initiator, ~~if appropriate~~ optionally, the remaining amount of the at least one dispersant, the total amount or, ~~if appropriate~~ optionally, the remaining amount of the at least one monomer and the main amount of the at least one water-soluble free radical initiator are then metered into the reaction mixture present in the reaction vessel, and the reaction mixture is heated to an end
10   reaction temperature T_E during the metering.

After the starting reaction temperature T_S has been reached or after the reaction mixture present in the reaction vessel has been left at this temperature for some time, the total amount or, ~~if appropriate~~ optionally, the remaining amount of the at least one monomer and the main amount of the at least one water-soluble free radical initiator are metered into the
15   reaction mixture. Advantageously, both metering operations begin simultaneously and take place in such a way that the polymerization reaction of the at least one monomer does not stop.

The metering of the at least one monomer is carried out as a rule in a time span T which, depending on the type and amount of the monomers or the cooling capacity of the
20   reaction vessel, is from 10 minutes to 20 hours, frequently from 0.5 to 5 hours or from 0.75 to 1.5 hours. The total amount or the remaining amount of the at least one monomer can be metered into the reaction vessel continuously, i.e. at a constant flow rate, batchwise, i.e. with a changing flow rate, stepwise, i.e. with interrupted flow or according to any desired predetermined flow rate profile. Of course, it is also possible to change the monomer
25   composition during the metering and thus to obtain the polymer particles which are two-phase, for example core/shell particles, or multiphase. Moreover, it is also possible to meter the monomers into the reaction vessel according to a gradient procedure familiar to a person skilled in the art [i.e. continuous change of the monomer composition].

The metering of the at least one water-soluble free radical initiator is carried out in
30   such a way that the main amount, i.e. ≥ 50, ≥ 60, ≥ 70, ≥ 80, ≥ 90, % by weight, based in each case on the total amount of the water-soluble free radical initiator, or even the total amount thereof is added during the monomer metering, advantageously beginning simultaneously with the monomer metering, and thus helps to maintain the polymerization reaction or to

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complete the reaction of the monomers. Portions of up to ≤30% by weight of the water-soluble free radical initiator can be initially taken before the monomer metering and portions of up to ≤20% by weight or ≤10% by weight of the water-soluble free radical initiator can be added to the polymerization mixture after the end of the monomer metering. The total

5   amount, the main amount or the remaining amount of the at least one water-soluble free radical initiator can be metered into the reaction vessel in principle continuously, batchwise, stepwise or according to any desired predetermined flow rate profile. Frequently, a portion of water-soluble free radical initiator is initially taken before the monomer metering and the resulting remaining amounts are added continuously simultaneously with the monomer

10   metering.

The metering of the monomers and of the water-soluble free radical initiator is frequently effected in such a way that, no later than from the time when 35% by weight of the total amount of monomers have been added to the reaction mixture, the metering of the monomers and of the water-soluble free radical initiator is effected in such a way that the

15   conversion of the monomers already metered into the reaction vessel is ≥80% by weight or even ≥90% by weight at all times, which can be monitored or realized, for example, on the basis of reaction calorimetry measurements.

If appropriateOptionally, the remaining amounts of demineralized water, of the at least one oil-soluble free radical initiator or of the at least one dispersant can be metered into

20   the reaction vessel in principle continuously, batchwise, stepwise or according to any desired predetermined flow rate profile. As a rule, the metering of, if appropriate optionally, the remaining amounts of demineralized water, of the at least one oil-soluble free radical initiator or of the at least one dispersant is effected within the time span ≤T. If the total amount of the at least one oil-soluble free radical initiator was not initially taken in the reaction vessel, the

25   metering of the residual amount thereof is advantageously effected within the time span within which ≤50, ≤40, ≤30, ≤20 or ≤10% by weight of the total amount of monomers were metered into the reaction mixture.

The heating process from T_S to T_E can in principle be started before, after or simultaneously with the beginning of the monomer metering. Frequently, the heating process

30   is started simultaneously with the beginning of the monomer metering. Advantageously, the heating process is carried out within the time span ≤T. The heating process can be carried out continuously, i.e. at constant heating rate, batchwise, i.e. with changing heating rate, stepwise, i.e. with interrupted heating rates [=phases of constant temperature] or according to

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any desired predetermined heating profile. It is advantageous if the heating of the reaction mixture is carried out by means of the polymerization energy liberated in the polymerization reaction of the at least one monomer. Conventional heating rates are ≥ 1, ≥ 5, ≥ 10, ≥ 20, ≥ 30 or $\geq 60°C./hour$ but also ≤ 100, ≤ 70, ≤ 50, ≤ 40, ≤ 30 or $\leq 20°C/hour$ and all values in between.

5   The process for heating the reaction mixture is particularly advantageously carried out in such a way that the temperature T_E is reached no earlier than at a time after which at least the main amount of the monomers, i.e. ≥ 50, ≥ 60, ≥ 70, ≥ 80, ≥ 90 or even 100% by weight of the total amount of monomer have been metered into the reaction mixture.

       The starting reaction temperature T_S is frequently from ≥ 30 to $\leq 120°C$ and often from 10 ≥ 50 to $\leq 110°C$ and from ≥ 70 to $\leq 100°C$, while the end reaction temperature T_E is frequently from ≥ 80 to $\leq \geq 200°C$ and often from ≥ 100 to $\leq 170°C$ and from ≥ 110 to $\leq 50°C$. It is advantageous if the end reaction temperature T_E is $\geq T_S +10°C$, $\geq T_S + 20°C$ or $\geq T_S + 30°C$.

       It is important that the novel process can optionally also be carried out in the presence of at least one reducing agent, which however is added to the reaction mixture no earlier than 15   after at least 50 or at least 60 or at least 70% by weight of the total amount of monomers have been metered into the reaction mixture. The total amount of optionally metered reducing agent is from 0.01 to 5, frequently from 0.5 to 3, often from 1 to 2, % by weight, based in each case on the total amount of monomers. The metering of the reducing agent optionally added can be carried out continuously, batchwise, stepwise or according to any desired 20   predetermined flow rate profile. Sulfur compounds having a low oxidation state, such as alkali metal sulfites, for example potassium and/or sodium sulfite, alkali metal hydrogen sulfites, for example potassium and/or sodium hydrogen sulfite, alkali metal bisulfites, for example potassium and/or sodium metabisulfite, formaldehyde sulfoxylates, for example potassium and/or sodium formaldehyde sulfoxylate, alkali metal salts, especially potassium 25   and/or sodium salts of aliphatic sulfinic acids, and alkali metal hydrogen sulfides, for example potassium and/or sodium hydrogen sulfide, salts of polyvalent metals, such as iron(II) sulfate, iron(II) ammonium sulfate, iron(II) phosphate, enediols, such as dihydroxymaleic acid, benzoin and/or ascorbic acid, and reducing saccharides, such as sorbose, glucose, fructose and/or dihydroxyacetone, can be used as corresponding reducing 30   agents.

       The novel free radical aqueous emulsion polymerization can be carried out in principle at a pressure which is less than, equal to or greater than 1 bar (absolute). It is advantageous if the pressure conditions during the initial introduction and during the

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metering/polymerization are chosen so that the reaction mixture does not begin to boil at any time during the novel process. The pressure may be 1.2, 1.5, 2, 5, 10 or 15 bar or may assume even higher values. Advantageously, the free radical aqueous emulsion polymerization is carried out at ≥ 1 bar (absolute) and under an inert gas atmosphere.

5   In addition, for achieving high monomer conversions or low residual monomer contents, it is advantageous if the reaction mixture is kept at the end reaction temperature T_E after the end of the monomer metering for at least a further 30 minutes with stirring. Depending on the reactivity of the monomers used for the polymerization, the subsequent reaction time is frequently ≥ 30 minutes and ≤ 5 hours or ≥ 45 minutes and ≤ 3 hours or ≥ 1

10   hour and ≤ 2 hours.

The novel process can of course also be carried out in the presence of further conventional assistants, for example free radical chain transfer compounds, polymer seed, antifoams, viscosity regulators, biocides, etc. Depending on their function, these assistants can be added to the initially taken mixture (for example polymer seed, antifoam), during the

15   metering (for example free radical chain transfer compounds, polymer seed) or after the end of the polymerization (for example biocides).

Free radical chain transfer compounds are usually used for reducing or controlling the molecular weight of the polymer obtainable by free radical aqueous emulsion polymerization. Substantially aliphatic and/or araliphatic halogen compounds, for example n-butyl chloride,

20   n-butyl bromide, n-butyl iodide, methylene chloride, ethylene dichloride, chloroform, bromoform, bromotrichloromethane, dibromodichloromethane, carbon tetrachloride, carbon tetrabromide, benzyl chloride or benzyl bromide, organic thio compounds, such as primary, secondary or tertiary aliphatic thiols, such as ethanethiol, n-propanethiol, 2-propanethiol, n-butanethiol, 2-butanethiol, 2-methyl-2-propanethiol, n-pentanethiol, 2-pentanethiol, 3-

25   pentanethiol, 2-methyl-2-butanethiol, 3-methyl-2-butanethiol, n-hexanethiol, 2-hexanethiol, 3-hexanethiol, 2-methyl-2-pentanethiol, 3-methyl-2-pentanethiol, 4-methyl-2-pentanethiol, 2-methyl-3-pentanethiol, 3-methyl-3-pentanethiol, 2-ethylbutanethiol, 2-ethyl-2-butanethiol, n-heptanethiol and its isomeric compounds, n-octanethiol and its isomeric compounds, n-nonanethiol and its isomeric compounds, n-decanethiol and its isomeric compounds, n-

30   undecanethiol and its isomeric compounds, n-dodecanethiol and its isomeric compounds, n-tridecanethiol and its isomeric compounds, substituted thiols, for example 2-hydroxyethanethiol, aromatic thiols, such as benzenethiol, ortho-, meta- or para-methylbenzenethiol, and all further sulfur compounds described in Polymer Handbook 3rd

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edition, 1989, J. Brandrup and E. H. Immergut, John Wiley & Sons, Section II, pages 133 to 141, but also aliphatic and/or aromatic aldehydes, such as acetaldehyde, propionaldehyde and/or benzaldehyde, unsaturated fatty acids, such as oleic acid, dienes having nonconjugated double bonds, such as divinylmethane or vinylcyclohexane, or hydrocarbons having easily

5   abstractable hydrogen atoms, for example toluene, are used. However, it is also possible to use mixtures of the abovementioned free radical chain transfer compounds which do not interfere.

The total amount of free radical chain transfer compounds optionally used in the novel process is as a rule ≤5, often ≤3, frequently ≤1, % by weight, based on the total amount of the

10   monomers to be polymerized.

In addition to the seed-free preparation method, the novel emulsion polymerization can be carried out by the polymer seed process or in the presence of an aqueous polymer seed dispersion prepared in situ, for establishing the polymer particle size. Processes for this purpose are known and are described in the prior art (cf. for example EP-B 40 419, EP-A 567

15   812, EP-A 614 922 and Encyclopedia of Polymer Science and Technology, Vol. 5, page 847, John Wiley & Sons Inc., New York, 1966). Thus, in the feed process, the prior art recommends initially taking a defined finely divided polymer seed dispersion in the polymerization vessel and then polymerizing the at least one monomer in the presence of the seed latex. Here, the seed polymer particles act as polymerization nuclei and decouple the

20   polymer particle formation and the polymer particle growth. During the emulsion polymerization, further aqueous polymer seed dispersion can be added to the reaction mixture. This results in broad size distributions of the polymer particles, which are often desired in particular in the case of polymer dispersions having a high solids content (cf. in this context, for example, DE-A 4213965). Instead of the addition of a defined seed latex, the

25   latter can also be produced in situ. For this purpose, for example, a portion of the at least one monomer and of the water-soluble free radical initiator is initially taken together with a portion or the total amount of the dispersant and heated to the starting reaction temperature T_S, a relatively finely divided seed forming. The actual polymerization is then carried out in the same polymerization vessel by the metering process described (cf. also DE-A 4213965).

30   What is of importance is the fact that the novel process can also optionally be carried out in the presence of dissolved heavy metal ions which may be present with various valencies, for example iron, manganese, copper, chromium or vanadium ions. Frequently, complexing agents, for example ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA), are also added and form complexes with the heavy metal ions and keep them in

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solution under the reaction conditions. Usually, the aqueous polymer dispersions obtained according to the invention have a content of dissolved heavy meal ions of $\leq$ 1 000 1,000 parts per million (ppm), often $\leq$500 ppm, frequently $\leq$100 ppm.

The polymers obtainable by the novel process may have glass transition temperatures

5   of from -70 to +150°C. Depending on the intended use, polymers whose glass transition temperatures are within certain ranges are frequently required. By a suitable choice of the ethylenically unsaturated monomers to be polymerized, it is possible for a person skilled in the art to prepare in a targeted manner polymers whose glass transition temperatures are in the desired range. If, for example, it is intended to use the polymers obtainable by the novel

10   process as contact adhesives, the composition of the monomer mixture to be polymerized is chosen so that the polymers produced have glass transition temperatures of <0°C, frequently $\leq$-5°C, often $\leq$-10°C. If, on the other hand, it is intended to use the polymers, for example, as binders in coating formulations, the composition of the monomer mixture to be polymerized is chosen so that the polymers produced have glass transition temperatures of from -40 to

15   +150°C, frequently from 0 to +100°C, often from +20 to +80°C. The same also applies to the polymers which are to be used in other applications.

The glass transition temperature T_g is understood as meaning the limiting value of the glass transition temperature, to which limiting value said glass transition temperature tends with increasing molecular weight according to G. Kanig (Kolloid-Zeitschrift & Zeitschrift fur

20   Polymere, Vol. 190, page 1, equation 1). The glass transition temperature is determined by the DSC method (differential scanning calorimetry, 20 K/min, midpoint measurement, DIN 53 765).

According to Fox (T. G. Fox, Bull. Am. Phys. Soc. 1956 [Ser. II] 1, 123 and according to Ullmann's Encyclopäedie der technischen Chemie, Vol. 19, page 18, 4th edition,

25   Verlag Chemie, Weinheim, 1980), a good approximation of the glass transition temperature of at most weakly crosslinked copolymers is:

$$1/T_g = x^1 1/T_g^1 + x^2/T_g^2 + \ldots x^n/T_g^n,$$

30   where x^1, x^2, $\ldots$ x^n are the mass fractions of the monomers 1, 2, $\ldots$ n and T_g^1, T_g^2, $\ldots$ T_g^n are the glass transition temperatures, in degrees Kelvin, of the polymers composed in each case only of one of the monomers 1, 2, $\ldots$ n. The T_g values for the homopolymers of most monomers are known and are mentioned, for example, in Ullmann's Encyclopedia of

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Industrial Chemistry, Part 5, Vol. A21, page 169, VCH Weinheim, 1992; further sources of glass transition temperatures of homopolymers are, for example, J. Brandrup, E. H. Immergut, Polymer Handbook, 1st Ed., J. Wiley, New York 1966, 2nd Ed. J. Wiley, New York 1975, and 3rd Ed. J. Wiley, New York 1989.

5   The polymer particles of the polymer dispersions obtainable by the novel process have number average particle diameters which as a rule are from 10 to 1 000 nm, frequently from 50 to 700 nm, often from 100 to 500 nm [determined, for example, by quasielastic light scattering (ISO standard 13 321)].

What is essential to the process is that the aqueous polymer dispersions obtainable by

10   the novel process can be stripped with inert gas and/or steam after the end of the monomer metering or advantageously after the end of the subsequent reaction time for removing any troublesome readily volatile components without a further heating process. The corresponding stripping processes are familiar to a person skilled in the art and are described, for example, in DE-A 2550023, DE-C 2759097, DE-C 2855146 or DE-C 2521780.

15   After cooling to room temperature, the aqueous polymer dispersions obtainable by the novel process can advantageously be used either directly or after corresponding stripping with inert gas and/or steam, for example as binders in adhesives, sealing compounds, plastics renders and surface coating materials and for modifying mineral binders. Furthermore, the corresponding polymer powders, which are likewise suitable as binders in adhesives, sealing

20   compounds, plastics renders and surface coating materials and for modifying mineral binders, are obtainable in a simple manner (for example freeze-drying or spray-drying) from the novel aqueous polymer dispersions.

Aqueous polymer dispersions which are virtually free of monomers or other volatile components and thus have little odor and low emissions are obtainable by the novel process--

25   in particular after stripping with inert gas and/or steam. The aqueous polymer dispersions obtainable according to the invention are therefore advantageously suitable for the preparation of solvent-free coating materials having low emissions, for example plastics dispersion renders, coating materials and in particular emulsion paints having low emissions and sealing compounds and adhesives. The process is distinguished in particular by the fact

30   that low residual monomer contents are obtained even without an additional chemical aftertreatment step which as a rule contaminates the aqueous polymer dispersions with additional secondary components. A corresponding aftertreatment reactor is thus no longer required. Furthermore, the fact that the polymerization times can be reduced and hence the

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polymer capacities increased by the monomer conversion rates optimized according to the invention is important.

The nonrestricting example which follows illustrates the invention.

5 Example

In a 6 l polymerization reactor having an MIG stirrer and heating/cooling means,

500 g	of demineralized water
1.0 g	of a 5% strength by weight aqueous solution of an EDTA Fe/Na salt (~~Dissolvine~~DISSOLVINE® E-FE-6, brand of Akzo Nobel)
10 4.0 g	of a 28% strength by weight aqueous solution of the sulfuric monoester of an ethoxylated C_{12}-fatty alcohol (~~Texapon~~TEXAPON® NSO IS, brand of Akzo Nobel)
112 g	of an aqueous polymer latex (prepared by free radical emulsion polymerization of styrene; polymer solids content 33% by weight)
15	having a weight average particle diameter of 30 nm
185 g	of a 5% strength by weight aqueous solution of itaconic acid
14 g	of tert-butyl peroxybenzoate (~~Trigonox~~TRIGONOX® C, brand of Akzo Nobel)

and 5% by weight of the feed I described below were initially taken at from 20 to 25°C (room
20   temperature) and heated to 95°C with stirring (90 rpm) and under a nitrogen atmosphere. On reaching 95°C, the remaining amount of feed I and the total amounts of feeds II and III were metered in with constant feed streams in the course of 90 minutes, with stirring and beginning simultaneously, the reaction temperature being caused to increase to 120°C by the liberated heat of polymerization, which was reached after about 60 minutes. During the
25   polymerization reaction, the pressure in the gas phase of the polymerization reactor was not more than 9 bar (gage pressure). Feeds I and II were fed to the polymerization reactor at the bottom via a common feed pipe.

Feed I is an aqueous emulsion prepared from:

600 g	of demineralized water
30 50 g	of a 10% strength by weight aqueous solution of sodium hydroxide
30 g	of a 28% strength by weight aqueous solution of ~~Texapon~~TEXAPON® NSO IS
80 g	of acrylic acid 20 g of tert-dodecyl mercaptan
1000 g	of styrene

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Feed II:

750 g of butadiene

5   Feed III:

280 g of a 12% strength by weight aqueous solution of sodium peroxydisulfate.

After the ends of feeds I to II, the polymerization mixture was stirred for a further two
hours at 120°C under a nitrogen atmosphere. Thereafter, the polymerization mixture was

10   cooled to 60°C and let down to atmospheric pressure. For removing unconverted butadiene,
the polymerization reactor was evacuated to 800 mbar (absolute) and left for one hour with
stirring at this pressure and at 60°C. Thereafter, the aqueous polymer dispersion obtained
was cooled to room temperature and the internal pressure of the reactor was allowed to
increase to atmospheric pressure.

15   The aqueous polymer dispersion obtained had a polymer solids content of 52% by
weight. The mean polymer particle diameter was 125 mm. The aqueous polymer dispersion
had a residual monomer content of 1 570 ppm of styrene and 840 ppm of acrylic acid.

The solids contents were generally determined by drying an aliquot amount of the
aqueous polymer dispersion at 140°C in a drying oven to constant weight. In each case two

20   separate measurements were carried out. The value stated in the respective examples is the
mean value of the two measured results.

The resulting residual amounts of styrene were generally determined by gas
chromatography, and the residual amounts of acrylic acid by means of HPLC.

The mean particle diameter of the copolymer particles was determined generally by

25   dynamic light scattering on a 0.005 to 0.01 percent strength by weight aqueous dispersion at
23°C by means of an Autosizer IIC from Malvern Instruments, England. The cumulant z-
average of the measured autocorrelation function is stated (ISO standard 13321).

Comparative Example

30   In a 6 l polymerization reactor having an MIG stirrer and heating/cooling means,

500 g	of demineralized water
1.0 g	of a 5% strength by weight aqueous solution of
	~~Dissolvine~~DISSOLVINE® E-FE-6

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4.0 g	of a 28% strength by weight aqueous solution of ~~Texapon~~TEXAPON® NSO IS	
112 g	of an aqueous polymer latex (prepared by free radical emulsion polymerization of styrene; polymer solids content 33% by weight) having a weight average particle diameter of 30 nm	
185 g	of a 5% strength by weight aqueous solution of itaconic acid	
42 g	of tert-butyl peroxybenzoate (~~Trigonox~~TRIGONOX® C)	

and 5% by weight of the feed I described below were initially taken at room temperature and heated to 95°C with stirring (90 rpm) and under a nitrogen atmosphere. On reaching 95°C, the remaining amount of feed I and the total amounts of feeds II and III were metered in with constant feed streams in the course of 90 minutes with stirring and beginning at the same time, the reaction temperature being caused to increase to 120°C by the liberated heat of polymerization, which was reached after about 50 minutes. During the polymerization reaction, the pressure in the gas phase of the polymerization reactor was not more than 12 bar (gage pressure). Feeds I and II were fed to the polymerization reactor at the bottom via a common feed pipe.

Feed I is an aqueous emulsion prepared from:

600 g	of demineralized water
50 g	of a 10% strength by weight aqueous solution of sodium hydroxide
30 g	of a 28% strength by weight aqueous solution of ~~Texapon~~TEXAPON® NSO IS
80 g	of acrylic acid
20 g	of tert-dodecyl mercaptan
1 000 g	of styrene

Feed II:

750 g of butadiene

Feed III:

220 g of a 15% strength by weight aqueous solution of sodium formaldehyde sulfoxylate.

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After the end of feeds I to III, the polymerization mixture was stirred for a further 2 hours at 120°C under a nitrogen atmosphere. Thereafter, the polymerization mixture was cooled to 60°C and let down to atmospheric pressure. For removing unconverted butadiene, the polymerization reactor was evacuated to 800 mbar (absolute) and left for one hour with

5   stirring at this pressure and at 60°C. Thereafter, the aqueous polymer dispersion obtained was cooled to room temperature and the internal pressure of the reactor was allowed to increase to atmospheric pressure.

The aqueous polymer dispersion obtained had a polymer solids content of 50% by weight. The mean polymer particle size was 130 nm. The aqueous polymer dispersion had a

10   residual monomer content of ~~3 550~~ 3,550 ppm of styrene and ~~1 910~~ 1,910 ppm of acrylic acid.

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